

**Structural Kinetics Study on Metal Deposition Using X-ray Scattering**

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Beamline(s): X22A, X25

**Introduction:** Very little is known about the kinetics of metal deposition and dissolution on microscopic scales. Previous investigations have utilized electrochemical methods, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and second harmonic generation (SHG). Although the electrochemical methods provide kinetic information they are not structural in nature. Conversely, the other methods (STM, LEED, and SHG) are structural but they are static in nature. A comprehensive understanding of the surface kinetic processes requires *in situ* and real time conditions, as well as atomic resolution.

X-ray scattering techniques, carried out with penetrating high-energy x-rays (3-4 mm of electrolyte) and a "drop" cell with its inherent fast response (cell resistance is minimized), make it possible to obtain real-time structural information on an atomic scale. In this report, we demonstrate structural kinetics study on a phase transition of underpotentially deposited Bi on Au(111) using x-ray scattering with drop cell.

**Methods and Materials:** A single crystal Au(111) electrode was prepared by flame annealing. A 0.1 M  $\text{HClO}_4$  solution containing 2.5 mM  $\text{Bi}_2\text{O}_3$  was used as the electrolyte and all potentials are referenced with respect to a Ag/AgCl electrode. The electrochemical cell was constructed from Kel-F. Wet  $\text{N}_2$  gases were brought into the cell chamber to minimize evaporation.

**Results and Discussion:** Figs. 1 shows the typical time course of electrochemical response and the x-ray scattering intensity during the transition between an ordered Bi-(2x2) adlayer and a disorder Bi adlayer with lower coverage, i.e. desorption. In this particular measurement the electrode potential was stepped at  $t = 0$  sec from  $E = 0.23$  V, where (2x2) phase exists, to  $E = 0.33$  V where the disordered phase exists (Further details on this system are reported in ref. 1-2.).

The current transient (Fig. 1(a)) shows a sharp spike followed by a broad peak, a typical type of response in nucleation-growth process. The spike is due to charging of the double layer and the anodic current peak is due to the disordering phase transition corresponding to the desorption of Bi. The X-ray reflectivity (Fig. 1(c)) at  $L = 0.4$ , which can be related to the Bi coverage, shows a gradual and linear-like increase up to 10 msec after the potential jump which is then followed by a more gradual increase, occurring over the next 20 msec. On the other hand, x-ray intensity at (0.5,0.5,0.2) in reciprocal space (Fig. 1(d)), which corresponds to the Bi-(2x2) structure, disappears in c.a. 6 msec after potential step.

These results prove that msec order structural change of electrode surface can be monitored by X-ray scattering method with "drop" cell in "nano"-scale resolution. Furthermore, they indicate that this nuclear-growth is not the disordered domain phase growth process, i.e., both nucleation-growth and phase transition proceeds quite independently.

**References:** 1. C. Chen, K. Kepler, A. Gewirth, B. Ocko, and J. Wang, "Electrodeposited Bismuth Monolayers on Au(111) Electrodes: Comparison of Surface X-ray Scattering Tunneling Microscopy, and Atomic Force Microscopy Lattice Structure", J. Phys. Chem., **97**, 7290, 1993.

2. K. Tamura, B. Ocko, J. Wang, and R. Adzic, "Structure of active adlayers on bimetallic surfaces: oxygen reduction on Au(111) with Bi adlayers", J. Phys. Chem. B, submitted.

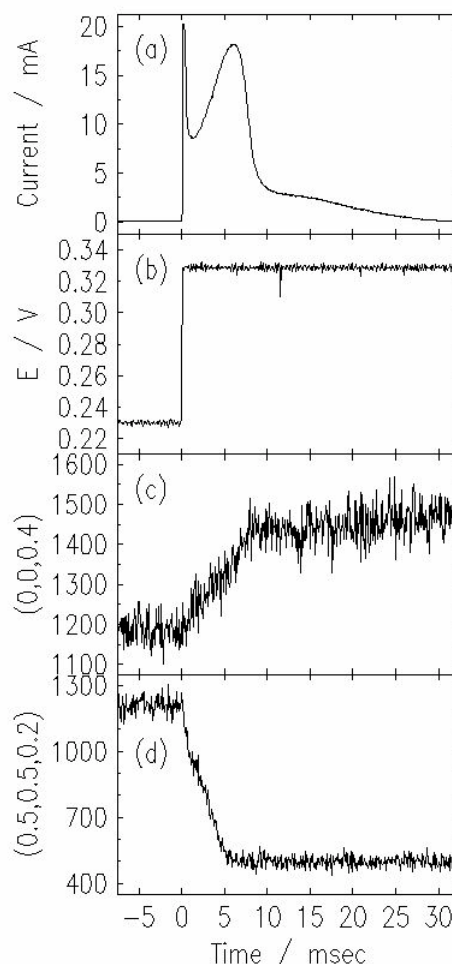


Figure 1. Time course of (a) current, (b) electrode potential, (c) x-ray reflectivity, and (d) x-ray intensity at (0.5,0.5,0.2) during (2x2)→disorder phase transition.